

## Historic, archived document

Do not assume content reflects current scientific knowledge, policies, or practices.





# METHODS FOR MANUFACTURING ACID-PRECIPITATED CASEIN FROM SKIM MILK

By CHARLES S. TRIMBLE, *associate dairy manufacturing specialist, Administrative Division*, and R. W. BELL, *senior dairy manufacturing specialist, Division of Dairy Research Laboratories, Bureau of Dairy Industry*

## CONTENTS

| Page                                                             | Page |
|------------------------------------------------------------------|------|
| Introduction.....                                                | 1    |
| Extent of manufacture and market in the United States.....       | 2    |
| Establishing a plant.....                                        | 2    |
| Volume and quality of skim milk required.....                    | 3    |
| Location of plant.....                                           | 3    |
| Equipment needed.....                                            | 4    |
| Cost of building and equipment.....                              | 8    |
| Cost of manufacture.....                                         | 9    |
| Manufacturing methods.....                                       | 10   |
| Types of casein produced by different methods.....               | 10   |
| General procedure in making any type of acid casein.....         | 10   |
| Lactic casein.....                                               | 17   |
| Sulphuric casein.....                                            | 22   |
| Hydrochloric (muriatic) casein.....                              | 24   |
| Yield of casein.....                                             | 28   |
| Uses.....                                                        | 29   |
| Marketing.....                                                   | 29   |
| Methods for determining the properties of commercial casein..... | 31   |
| Moisture content.....                                            | 31   |
| Ash content.....                                                 | 32   |
| Adhesive strength.....                                           | 32   |
| Solubility.....                                                  | 33   |
| Viscosity.....                                                   | 33   |
| Acid intensity—pH value.....                                     | 34   |
| Free-acid value.....                                             | 34   |
| Fat content.....                                                 | 34   |
| Foaming tendency.....                                            | 35   |
| Conclusions.....                                                 | 36   |
| Literature cited.....                                            | 36   |

## INTRODUCTION

The increasing volume of skim milk in dairy-products plants of the United States makes it essential not only to develop new ways of utilizing skim milk but to enlarge its present uses.

The manufacture of casein in the United States has increased markedly in the last few years, almost twice as much skim milk having been utilized for this purpose in 1936 as was used in 1932. To enlarge this outlet, however, calls for a greater knowledge, on the part of casein producers and users, of the properties which casein must have to insure its greater adaptation and utilization in paper coating, and in other industries. While the manufacture of casein is not difficult, special care is required in its manufacture in order that it may have the desired qualities.

The purpose of this circular is to make information of practical value available to present and prospective manufacturers of acid-precipitated casein. The manufacturer should know how to make casein both from the standpoint of quality and from the standpoint of economy.

## EXTENT OF MANUFACTURE AND MARKET IN THE UNITED STATES

Except for relatively small quantities of edible or other special caseins, practically all domestic casein is made with the aid of lactic, sulphuric, or hydrochloric acid, as the precipitating agent. Acid-precipitated casein is manufactured principally in New York and Vermont in the East, in Wisconsin and Illinois in the Middle West, and in California and Idaho in the West. During the last few years these 6 States have produced from 85 to 95 percent of the total annual output in this country. The quantity of casein made and the number of plants engaged in its manufacture have fluctuated from year to year as shown in table 1.

TABLE 1.—*Number of plants engaged in manufacture of casein and quantity manufactured in the United States, quantity imported, and domestic market (production plus imports), in the 10-year period 1927-36*<sup>1</sup>

| Year      | Domestic production |                   | Quantity imported | Domestic market (production plus imports) |
|-----------|---------------------|-------------------|-------------------|-------------------------------------------|
|           | Plants              | Quantity reported |                   |                                           |
|           | <i>Number</i>       | <i>Pounds</i>     | <i>Pounds</i>     | <i>Pounds</i>                             |
| 1927..... | 130                 | 18,033,000        | 24,209,000        | 42,242,000                                |
| 1928..... | 140                 | 22,151,000        | 28,728,000        | 50,879,000                                |
| 1929..... | 214                 | 30,537,000        | 27,583,000        | 58,120,000                                |
| 1930..... | 316                 | 41,965,000        | 18,499,000        | 60,464,000                                |
| 1931..... | 222                 | 35,335,000        | 3,503,000         | 38,838,000                                |
| 1932..... | 195                 | 24,428,000        | 1,201,000         | 25,629,000                                |
| 1933..... | 244                 | 24,087,000        | 8,142,000         | 32,229,000                                |
| 1934..... | 368                 | 37,331,000        | 1,491,000         | 38,822,000                                |
| 1935..... | 340                 | 37,368,000        | 3,230,000         | 40,598,000                                |
| 1936..... | 552                 | 46,140,000        | 16,209,000        | 62,349,000                                |

<sup>1</sup> Compiled from dairy statistics of the Bureau of Agricultural Economics.

After the increase in the tariff rate on casein, from 2.5 cents to 5.5 cents per pound, which went into effect on June 17, 1930, there was a sharp decline in imports. However, more than 8 million pounds came in over this barrier in 1933, and in 1936 the amount was 16,209,000 pounds. In 1936, the last year for which data are complete, the indicated domestic market reached the record figure of 62,349,000 pounds. While this is much more casein than has been produced in the United States in any calendar year, there is no doubt that the plant capacity of the country is ample to take care of consumption demands.

### ESTABLISHING A PLANT

Casein, as commonly made, is not a food product. When conditions are such that there is an oversupply of food products made from skim milk and prices for these products are low, the diversion of skim milk into casein may be of material benefit in stabilizing and strengthening markets for other skim-milk products. In sections where such food products cannot be made or marketed readily, the manufacture of good-quality casein should be given serious consideration as a means of utilizing skim milk to advantage. In

many cases, also, it is not advisable to equip small dairy-products plants with expensive condensing or desiccating machinery when casein equipment can be installed at a relatively small cost. In a plant equipped for making products from skim milk, the special equipment needed for producing casein is comparatively inexpensive and increases the flexibility of operation. It is often advisable to arrange equipment and operations so that the dairy-products plant can be changed quickly from the manufacture of one product to another product without materially affecting the operating efficiency. The more flexible the dairy-products plant, the easier it is to take advantage of fluctuating market conditions.

Casein can be made during any season of the year. When ordinary care is exercised in storing the finished product, it can be kept for months without deterioration. Therefore, casein can be made in isolated sections because the distance from market is not as important as in the marketing of perishable dairy-food products.

#### VOLUME AND QUALITY OF SKIM MILK REQUIRED

The volume of skim milk necessary for successful operation of a casein factory is greater when casein is the only product made than when other skim-milk products are made also. If casein is the only product to be made, it will probably be necessary to process at least 25,000 pounds of skim milk daily, and even larger quantities are advisable. The cost of manufacture per unit amount of casein should decrease with an increase in the daily volume of business. When other products are made in a plant that is equipped to make casein, then casein can be made from a small daily volume of skim milk at very little additional cost for labor and power. In such a plant the making of casein may be advisable when only 5,000 to 6,000 pounds of skim milk per day are available for its manufacture.

Sweet, clean, unpasteurized skim milk, fresh from the separator, is desirable if high-grade uniform casein is to be made. Such factors as fermentation, and excessive fat and foam in the skim milk, may deleteriously affect the quality of the finished product.

#### LOCATION OF PLANT

If the volume of skim milk available is large enough to justify the establishment of a casein factory, the location of the building should be given careful consideration. A separate building is advisable for large-scale production. This building should be convenient to the main plant to facilitate transferring the skim milk and supplying the power, the steam for heating and drying, and the large amount of water required in the washing process. Adequate facilities for sewage disposal should be available, as well as facilities for shipping the casein and receiving coal and other supplies. When the amount of casein to be made does not warrant the erection of a separate building, the space allotted to casein manufacture should be separated from other departments as much as possible and be ample for all purposes.

## EQUIPMENT NEEDED

Practically the same equipment is needed in making any type of casein. This equipment is neither extensive nor expensive. If it is not used for a period of time, depreciation costs will be less than with the equipment employed in making most other milk products. The addition of a few special units to the facilities of a modern dairy-products plant will equip the plant for the manufacture of casein by ordinary methods. It is desirable to provide equipment which is of the right type and of sufficient capacity to facilitate quality production.

The equipment listed below is sufficient for processing 10,000 pounds of skim milk daily:

- One 1,000-gallon tank for storing skim milk.

- Two 5,000-pound (or one 10,000-pound) milk or cheese vats, or unlined wooden vats, for holding the skim milk for precipitating and washing the curd.

- One 1,000-gallon tank for storing whey when lactic casein is made.

- Facilities for determining acidity and bromocresol green indicator paper.

- Two 2-inch centrifugal pumps for skim milk and whey.

- One or two curd presses with dividing boards and press cloths.

- One curd mill of the shredder-beater type.

- One hundred and eighty standard drying trays, 30 inches square, with 8-mesh to 10-mesh galvanized-iron screening.

- Six tray trucks.

- One drying tunnel 22 feet long, 5 feet high, and 32 inches wide.

- One high-speed fan, equipped with motor for circulation of heated air, 30 to 35 inches in diameter.

- Radiators or steam coils for drier, together with steam trap for condensation.

- One recording thermometer to assist in control of temperature of air in drier.

- One grinder.

- Miscellaneous small equipment such as strainers, pulleys, steam piping, valves, steam and water hose, rakes or paddles, thermometers, pails, bags, and scales for use in weighing dried casein.

More vat space will ordinarily be required in making lactic casein than in making other acid-precipitated caseins, and extra containers will be required for holding the whey to be used for starter. In making hydrochloric and sulphuric casein, containers in which to dilute the sulphuric or hydrochloric acid will be needed; also a supply of acid and other minor accessories will be necessary.

If wooden vats instead of metal cheese vats are used, often such vats may be constructed at the casein factory at less cost than when purchased as complete units. Redwood, cypress, pine, or other suitable wood can be used. The vats should be made of 2-inch stock and should be braced with rods or long bolts under the bottom and along the sides. The bottom should slope toward the outlet to facilitate drainage. Steam lines for delivering steam for heating the skim milk should be installed, either along the sides of the vat or overhead. Open vats in which direct steam is admitted are commonly used in making casein, although jacketed vats afford better control of temperatures, and can often be used to advantage.

The tanks for storing the skim milk and whey should be placed where they can be kept clean and sanitary. Either metal or wooden vats may be used.

The curd presses (fig. 1) should be substantially constructed so that sufficient pressure can be applied to the wet curd. It is cheaper to expel the moisture mechanically than to vaporize it by means of heat. A properly pressed curd mills and spreads more easily than a poorly pressed curd. Special mechanical presses (fig. 2) are now available for large-scale production. When the quantity of casein made justifies the extra investment, these special presses save much time and labor. The pressing of the curd then becomes a continuous process. Their operation is so effective that the pressed curd has a moisture content of approximately 50 percent.

Burlap-sacking material is commonly used as press cloths in casein plants, but its use for this purpose is not advisable, as it is hard to clean and keep clean. A cloth that is somewhat heavier and closer woven than burlap is more satisfactory. Heavy white duck (no. 10 size), light-weight canvas, or similar cloth material will give better service than burlap. Some companies make a specially woven heavy cloth which can be obtained in any size desired and is very satisfactory.

A shredder-type curd mill will give good service except when cooked-curd casein is made.

It is important that galvanized screening be used on the drying trays as ordinary screening soon rusts and small metal particles get into the finished product. Copper screening is durable but will often impart a green color to the dried casein. During the slack season of production the screens should be shellacked or varnished to preserve them and lengthen their life.

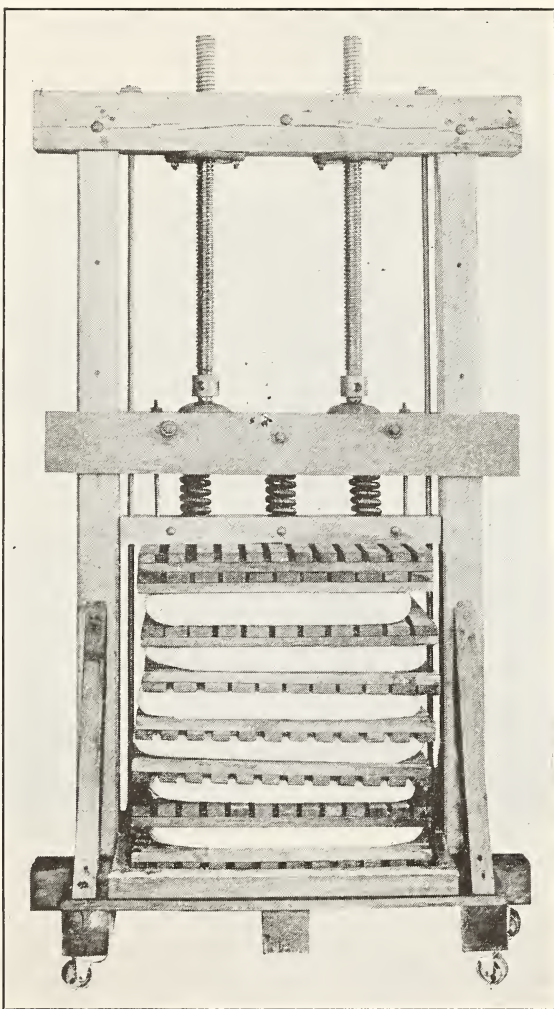


FIGURE 1.—Casein curd press (batch type).

A tunnel of the dimensions given for a 10,000-pound plant is large enough for drying the casein from 15,000 pounds of skim milk. A drying tunnel (fig. 3) of this size, however, is more satisfactory than a smaller one as it facilitates the work and allows for expansion. It is often desirable from the standpoint of economy of space and construction to have two tunnel driers built together, with one wall in common. The tunnel or tunnels should be located where they will be convenient but not in the way, and room should be provided for installing additional tunnel units if the volume of business makes this necessary in the future. The most advantageous place for the

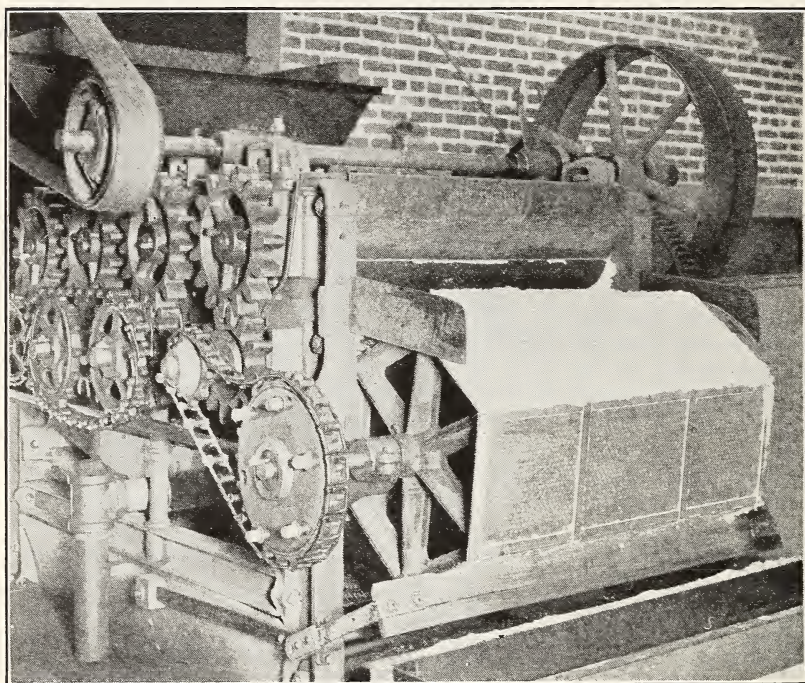


FIGURE 2.—Casein curd press (continuous type).

installation of the tunnel in a 2-story building is usually on the second floor. A continuous drier suitable for large plants is shown in figure 4.

The drying of casein is the largest single cost item in the manufacturing process. An improperly designed and constructed drying unit is expensive to operate, as it requires too much power and heat and takes too long to properly dry the casein, and the quality of the finished product may be deleteriously affected. The construction of the drier, therefore, should be given careful attention, for a properly constructed drier will, because of savings effected, be the most economical in the end. The drier should be not only air-tight in construction, but also insulated to conserve and retain heat. The inside of the tunnel should preferably be lined with metal rather than with wood. The steam pipes leading to the heating coils should

be insulated. There should be ample room at both ends of the tunnel to facilitate handling the trucks in filling and emptying the drier.

Many of the drying tunnels now in operation are built 6 feet high, instead of 5 feet as given on page 4. The added height is more convenient for handling the loaded trucks, and when space permits is desirable. Correct and controlled air circulation is an important factor in the production of high-grade casein. The fan should be of the high-speed type to insure efficient circulation of air. The floor of the room, if airtight, can be used as the floor of the tunnel. A recording thermometer will aid in safeguarding against too high a drying temperature.

The grinder may often be dispensed with, especially on small-scale production. Some jobbers and users of casein prefer to do their own grinding, and so many manufacturers sell their product unground. On large-scale production it is advisable to have a grinder that can be adjusted to grind the dried casein into particles of any desired size. Either a burr-type or roller-type grinder may be used. With the roller type the casein passes through adjustable steel rolls, where it is ground to the desired fineness. The casein ground in such grinders is usually more uniform in particle size than that ground in a burr-type machine. The latter type, however, is generally somewhat cheaper in price and for a small plant will give satisfactory service. Magnetic separators that remove metallic material, such as nails, bolts, or bits of screen, that may have gotten into the casein, are used by some jobbers. While most of the casein marketed is ground to pass through a 20- to 30-mesh screen, some users require a more finely ground product, or one that will pass through an 80- to 100-mesh screen. The casein factory with a direct market outlet should be equipped with an adjustable grinder.

As with the wooden vats mentioned, it is often possible for a casein manufacturer to make other equipment at substantial savings. Trays and tray trucks, and often the drying tunnels may be so made at less expense than when purchased as complete units. It is advisable, however, to consult experienced casein manufacturers and dealers as to the best equipment to make or purchase. Many of the manufacturers, dealers, and dairy-supply companies are in a position to furnish valuable information on the proper equipment and its correct

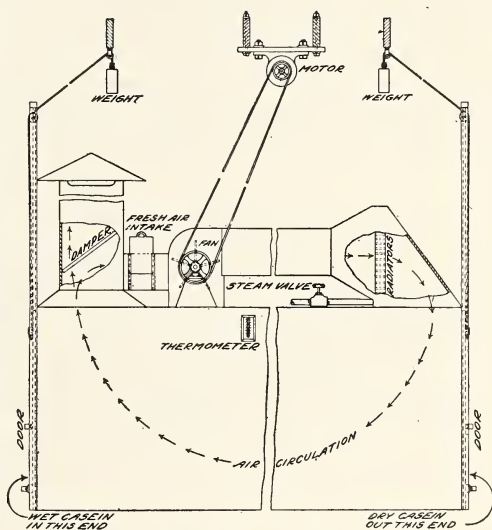


FIGURE 3.—Casein drier (tunnel batch type).

installation, and to solve the engineering problems involved, in order to obtain the most efficient operation.

As long as the precipitating and washing operations are carried out in vats and the tunnel method of drying prevails, the equipment needed for either a small or a large plant will not vary much from that listed on page 4, other than in the size and number of units. It is true, no doubt, that the finished product made by special equipment and processes will be more uniform in quality than that made by the ordinary hand methods.

The drying should be done at the original plant whenever possible, since the wet pressed curd deteriorates quickly and an inferior finished product may result if the curd is not dried promptly.

The equipment installed in the usual casein factory, while it need not be elaborate, should always be sufficiently high grade and so arranged that the different units can be kept in a clean and sanitary condition. Good equipment properly arranged, and then kept clean, is an asset of material importance in the making of a quality product. In general, a higher standard of sanitation prevails and better equipment is used in plants where uniformly high-quality casein is made than in those plants which produce an inferior grade.

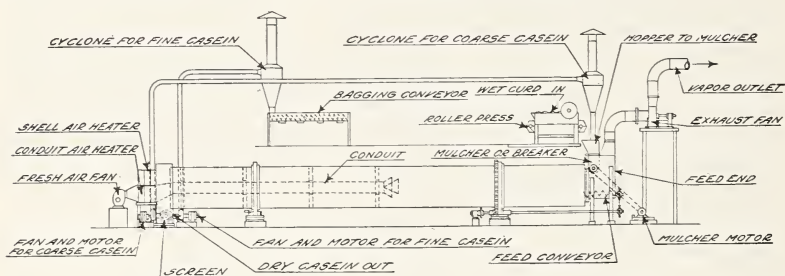


FIGURE 4.—Casein drier (revolving-drum continuous type).

Courtesy Louisville Drying Machine Co.

#### COST OF BUILDING AND EQUIPMENT

It is not possible to give cost figures for building and equipment that would apply to all sections or local conditions.

Estimates on prices of equipment received from casein dealers and jobbers of casein equipment vary within rather wide ranges. The estimated price of equipment necessary for processing 5,000 to 10,000 pounds of skim milk daily ranged from \$800 to \$1,500 f.o.b. origin. This wide range is due to differences in quality and kind of equipment listed. For example, wooden vats may be purchased or built for from \$100 to \$150 each, while a metal cheese vat would cost from \$300 to \$350. Such vats would be much higher in price if they were equipped with mechanical agitators. Curd presses of the usual design range in price from \$85 to \$175, curd mills from \$100 to \$300, screen trays from 60 cents to \$1.10 each, and complete drying tunnels from \$400 to \$800.

Cost estimates obtained from casein manufacturers also vary within rather extreme ranges. Some managers of plants in which 8,000 to 12,000 pounds of skim milk are processed daily placed the total cost of the equipment only at from \$700 to \$800. Others who process about the same amount of skim milk gave a figure materially higher,

ranging from \$1,200 to \$1,500, and even more. These figures are all for factories which operate as branch departments of a milk-products plant, and do not include charges for transportation, installation, and building space in the main plant, or new construction. As already stated, the total cost of necessary equipment can often be reduced when a plant is able to build or have much of its equipment made locally. It is false economy, however, to attempt to manufacture casein with inadequate or poorly constructed equipment. Not only is operating efficiency impaired, thus raising manufacturing costs, but the quality of the finished product may also be harmed. Sufficient capital should be provided to supply not only adequate equipment, but also to provide for its proper installation and arrangement in the plant.

On the basis of a survey in 1930 of a large number of casein factories operating in various sections of the country, the total cost of complete equipment and materials, and installation, exclusive of building space, varied from \$1,500 to \$2,500 for the smaller plants, and from \$3,500 to \$4,500 for the larger plants, depending upon the existing local conditions and market prices. These figures are only approximations, but indicate what the prospective manufacturer of casein would have to invest in order to start a casein factory in conjunction with a milk-products plant.

A separate building or an addition to an older building would, of course, add to the cost estimates given, and the prospective manufacturer would have to be governed by previous experience as to the building materials and the size and type of building best suited for local conditions and needs. Advice from reliable sources should be sought and when at all feasible, an inspection visit made to several efficiently operated casein factories before construction is started and equipment purchased or installed. Equipment such as special driers or presses or patented machinery is more expensive than the equipment listed above. A few of the larger casein manufacturers in the United States have invested \$40,000 to \$50,000 in special equipment and machinery.

### COST OF MANUFACTURE

It is difficult to give exact figures on the cost of manufacturing casein. The costs of equipment and labor vary in different parts of the country, as does also the price paid for, or the value assigned to, the skim milk. The amount of skim milk processed is an important factor. According to a report of the United States Tariff Commission, the cost of manufacturing casein in 1922 ranged from 2.49 to 8.23 cents per pound in 16 plants, with a weighted average of 4.68 cents. Estimates recently obtained from a number of manufacturers give 1 cent per pound of finished product as the cost of drying. This is the largest single cost item, other than that for the skim milk. This fact emphasizes the need for an efficient drier. The cost of water for washing the curd, of steam for heating the skim milk, of power for operating the blower and the grinder, the cost of labor and of acid, are all direct cost items which must be taken into consideration. Expenses such as depreciation of equipment and building, interest, taxes, insurance, etc., are indirect cost items that must be considered in arriving at any exact figures of

manufacturing cost. No detailed data are available, but it is probable that with properly designed, labor-saving equipment and a sufficient volume of skim milk, the actual cost of manufacturing casein need not exceed 2 cents per pound, exclusive of the value of the skim milk. Some factories have been able to lower manufacturing costs by purchasing skim milk from nearby creameries and manufacturing all their casein at one large central plant.

## MANUFACTURING METHODS

### TYPES OF CASEIN PRODUCED BY DIFFERENT METHODS

Commercial casein, except for minor amounts of rennet casein and specially prepared caseins, is practically all acid-precipitated casein. Acid casein is casein which has been precipitated through the action of lactic acid formed in milk, with or without the use of a starter, or by the addition of an acid, usually either hydrochloric or sulphuric acid. Therefore, in commercial practice there are three general groups of acid casein, namely, lactic, hydrochloric (muriatic), and sulphuric. Within these groups are types which possess characteristic properties. Both types of commercial lactic casein, self-soured and starter, are commonly found on the market. The principal types of hydrochloric (muriatic) casein manufactured are pressed curd, cooked curd, and grain curd. In the case of sulphuric casein, the pressed curd and cooked curd types are the most common. Within all three groups, however, products of the desired quality which differ but little in general characteristics can be made by proper control of the process and if necessary by suitable modifications in the operating conditions. From the standpoint of practical utilization all types of acid casein will, when made by proper methods, be interchangeable.

Rennet casein is made, not with the aid of an acid as the precipitating agent, but with rennet, a commercial preparation which contains the enzyme rennin, and is of relatively minor importance in the present casein industry. There are a number of other methods of manufacturing casein, but they are not used except in relatively few instances. The greater cost of precipitating agents other than those mentioned limits their application in the industry. The demand for casein that is made with special equipment and methods for a special purpose is limited, and such caseins naturally command a higher market price. Examples of these are edible, powdered, chemically pure, and vitamin-free caseins. Casein can be made from sweet buttermilk. The quality is generally considered inferior to that made from skim milk. Sour buttermilk from neutralized high-acid cream cannot be satisfactorily utilized for making casein. Mixing buttermilk with the skim milk will lower the quality of the casein.

### GENERAL PROCEDURE IN MAKING ANY TYPE OF ACID CASEIN

In general, the principles involved in making all acid-precipitated caseins are similar. The casein of the skim milk is precipitated in the presence of heat by the addition of an acid or by fermentation.

The precipitating temperatures used, the kind and amount of starter or the dilution and amount of acid added, the method and

speed of agitation while mixing, the size of curd particle obtained, the length of time the whey is left in contact with the curd, and the amount of washing that the curd receives all affect the properties of the finished product. In many casein factories these factors are the very ones that are not closely controlled, and they all vary within rather wide ranges in different factories or even in the same factory. The lack of uniformity that exists in much of the casein made may be attributed to a lack of more definite control of these important factors.

It is important that the workers assigned to make casein should be familiar with the basic principles involved in its precipitation. Too often inexperienced and low-paid workmen are delegated to make this product. Instances could be cited where equipment and material were of the best, yet solely because of a lack of proper understanding on the part of the maker the final product was inferior.

With acid caseins, other than those of the cooked-curd type, once the curd has been precipitated, the rest of the handling and manufacturing process is almost identical, and unless otherwise noted will be substantially as described under the headings: Draining, washing, pressing, milling, spreading, drying, grinding, packing, and storing.

#### IMPORTANCE OF ACIDITY CONTROL

Casein is a normal protein constituent of all milk and occurs in colloidal solution in combination with calcium. It is precipitated by lactic acid, which is formed naturally from the milk sugar by fermentation, and is also precipitated by the addition of an acid or a salt. Casein, as stated by Clark (2)<sup>1</sup> and others, is an amphoteric electrolyte whose isoelectric point or range in terms of Sorenson's scale has been shown to be at or near pH 4.6. In equilibrium with an environment at its isoelectric point, casein is considered to be uncombined; at pH values higher (less acid) than 4.6 it is combined to some extent with base; at pH values lower than 4.6 it is combined to some extent with acid. Casein is least soluble at or near its isoelectric point, pH 4.6. This is the acid intensity at which, theoretically, the maximum precipitation of casein as casein occurs, uncontaminated with its compounds except so far as they are carried down by occlusion and adsorption.

In the commercial adaptation of this principle, in order to guard against manufacturing losses the casein curd should be porous, resilient, preferably granular, and should retain these characteristics throughout the washing and handling operation. In order to obtain a curd of this character which may be readily washed and handled, it is usually necessary under the manufacturing methods used in most plants to bring the reaction to an intensity somewhat more acid than that corresponding to the isoelectric point—that is, a pH value below that of the isoelectric point must be reached. In work done by the Bureau of Dairy Industry with all types of acid casein, the end point at which the curd seemed to be in the most workable condition was at a pH value of approximately 4.1. With some special processes pH values nearer the isoelectric point will

<sup>1</sup> Italic numbers in parentheses refer to Literature Cited, p. 36.

produce a workable, good-quality curd and one that can be readily handled. However, under ordinary manufacturing methods the end point that will aid most in obtaining best results is approximately pH 4.1. In determining this end point under commercial conditions, exact methods of determination are necessary, as well as a physical examination of the curd.

The amount of acid necessary to attain this end point, at which the most desirable type of curd forms, depends on such factors as the initial acidity of the skim milk, the composition of the skim milk, the precipitation temperature, kind and dilution of acid, methods of adding and mixing the acid with the skim milk, and methods of handling the precipitated curd. The variety of these factors indicates the need of using exact methods for attaining the optimum end point. For example, if the precipitating temperature is high, a clear whey will be obtained after a relatively small amount of acid has been added. The curd can be easily drained but will not be porous, resilient, or granular and, therefore, cannot be effectively washed. Either insufficient acid or an excess of acid is detrimental to the production of curd that will make a finished casein of the highest quality.

In practice the quickest and most satisfactory method for determining when the desired acidity of the casein whey has been reached is the use of bromocresol green indicator paper ( $\gamma$ ). Since the pH value is a convenient means of expressing hydrogen-ion concentration, the use of strips of this indicator paper is a simple means of determining the intensity of the acidity of the whey. A strip of the paper is dipped in the whey and placed on a window pane not in direct sunlight. Its color viewed by transmitted light is then compared with a standard set of colors viewed by reflected light. The standard colors correspond to pH values within the acidity range near the desired end point. The observation must be made quickly, as the color of the wet indicator paper changes on standing. In this manner the intensity of the acidity of the whey can be determined quite accurately. After some practice with this method an operator can gauge the end point reached within 0.1 pH unit of the actual pH value of the whey as determined by a potentiometric titration. Values ranging from approximately pH 3.8 to 5.2 can be determined by this method. The color gradations which correspond to these values range from a bright yellow (pH 3.8 and below) to a deep blue (pH 5.2 and above). The paper is greenish yellow if the acidity of the whey is at or near pH 4.1, the most desirable end point. Deeper shades of green gradually turning to blue indicate higher (less acid) pH values. Colored paper standards and bromocresol green indicator paper are commercially available. The color standards should be used only for comparative purposes.

Bromocresol green paper can also be used to determine the acid intensity of the wash waters. When the water imparts a green or yellowish-green color to the paper (pH 4.3 to 4.6), it is sufficiently acid to use for washing purposes. A blue color shows that the wash water should be acidulated for most satisfactory results.

The desired end point of casein whey can also be determined with sufficient accuracy for practical purposes by titrating a sample of the whey against a standard alkali solution with phenolphthalein

solution as the indicator. However, the titratable acidity value at the optimum end point varies with the different methods of making casein; for example, it is greater in whey of lactic casein than in whey of grain-curd hydrochloric casein, of the same pH value. This apparent difference in the results of the titration and color methods can be understood when it is stated that the titratable acidity, which is expressed in percentage of acid is a measure of the quantity of acid and not a measure of acid intensity. For ordinary commercial purposes, however, when the conditions are uniform from day to day, the titratable acidity of the whey will be found to be a satisfactory index of when the desired end point is reached. However, it is not as quick or convenient a method as the use of bromocresol green paper.

Experienced makers are also able, by a physical examination of the curd, to gage rather closely whether the proper acid intensity has been attained. Usually, when the curd is at or near the optimum end point it will have a characteristic "feel", and will not mat when squeezed together in the hand. Another, though less reliable, indication of proper precipitation is the presence of a clear, greenish-colored whey. The reaction of samples of the curd to wash waters of different temperatures is also an indication of whether sufficient acid intensity has been attained. These factors, together with proper testing, should all be considered in controlling the acidity of the whey.

#### DRAINING

Regardless of which group or type of casein is being made, the whey should be quickly removed as soon as suitable precipitation has taken place and the curd has settled for a few minutes. The longer the curd stays in contact with the whey, the more difficult it will be to wash the curd free of acid, milk, sugar, and salts. For this reason a casein curd left in whey too long tends to be more insoluble after drying. As rapid removal of whey is essential, adequate means for its removal should be provided. Often, the whey pump is not large enough to take the full flow of the whey from the vat. Many plants are handicapped in disposing of whey because of regulations prohibiting the draining of whey into the sewage system or because the sewage facilities are inadequate to handle a large volume. In other communities it is not permissible to drain some kinds of casein whey into a running stream. Where the whey is to be saved for farm use or for further processing, the tanks provided for holding it should be large enough to hold all the whey from a day's make; otherwise drainage from the casein curd may be retarded.

In draining curd, especially if it is of the granular type, the curd is first pushed back from the outlet end of the vat and allowed to settle, just as in cheese making. A strainer is then inserted in the gate valve from the inside, and the valve is opened full width. When a sloping bottom has not been built in the vat the outlet end of the vat should be lowered to facilitate drainage. A burlap sack tied over the gate valve will prevent the loss of small particles of curd. A coarse strainer of heavy wire or a board inserted in the vat about 3 or 4 feet from the outlet and extending across the vat, will also serve to hold the curd back and facilitate drainage.

## WASHING

Effective washing of the curd is extremely important in making any type of casein. In the precipitating process soluble constituents of the skim milk are carried down with the curd, and unless the curd is washed thoroughly a considerable portion of the acid, soluble salts, and milk sugar present will be included in the final product. Inadequate and ineffective washing of a casein curd lowers the quality of the finished product. Casein made from such curd is relatively high in free acid, sugar, and ash content, and is often discolored during the drying process because of the presence of these substances. A high fat content in the skim milk may also cause discoloration during drying. Since large amounts of water are required in the washing of the curd, an adequate supply should be available. The acidity or alkalinity of the water should be determined by titration or with litmus paper and corrections made if necessary. The water pipe or hose lines to the vats should be sufficiently large—preferably  $1\frac{1}{4}$  to 2 inches in diameter—so that the drained curd can be quickly covered with water. The sooner the curd is washed the better. Where only a small stream of water is available, too much time is required to wash the curd adequately, and the tendency is to neglect the washing operations.

When the whey has drained from the curd, about as much wash water as there was whey should be added to the curd, the mixture stirred thoroughly, the curd allowed to settle for a few minutes, and the water drained off. This process should be repeated as many times as necessary. The temperature of the wash waters will be discussed under each manufacturing method, but generally the last washing should be with cold water (about 60° F.) in order to cool the curd and retard further acid development in the press. All curds should be washed at least twice. Some manufacturers of the best quality of casein make a practice of washing the curd from 3 to 6 times. After the final washing, when the visible free water has been drained off, the curd is ready to be pressed. The vat should be thoroughly cleaned and washed after being used.

## PRESSING

The washed, drained curd is usually shoveled from the vat into the press cloths. One of the cloths is placed over the press form, which is set on a drain board on the bottom of the press. Loose, wet curd is packed down into the cloth until the form is full, then the form is removed, and the cloth is lapped over the mass of curd. On this wrapped wet curd is placed another drain board, and the operation just described is repeated until all of the curd is stacked in the press. Care should be taken to have the curd stacked evenly, otherwise some of it may be pushed out of line when pressure is applied. With the ordinary screw-type, vertical press, the curd is pressed into solid cakes, about 30 inches square and 3 to 4 inches thick. When pressure is first applied a large amount of water is expelled. This is free moisture which contains small amounts of the soluble constituents of the skim milk. Pressing is, therefore, a refining as well as a dehydrating process. The pressure should be increased at intervals. The usual factory practice of pressing over-

night will produce solid cakes of curd that contain about 50 percent of moisture and will mill readily. Properly pressed curd yields a fine, mealy product when milled, one that will not become lumpy on the drying trays. If insufficient acidity was developed in the skim milk-whey mixture during precipitation, the curd will stick to the press cloths.

All press forms, drain boards, and press cloths, should be washed and scalded as soon as possible after being used. The press cloths should be hung outdoors to dry when not in use.

#### MILLING AND SPREADING

After the curd has been pressed for several hours or overnight into solid cakes, it should be milled without delay. The cakes of moist curd will soon mold if allowed to stand in a warm room. Unless the curd is of the cooked-curd type and hard or "rubbery", it can be milled readily with a shredder-beater type of curd mill. The milled curd should be firm and mealy. It should be spread smoothly and evenly in a thin layer on the drying trays. Hand spreading is commonly practiced, though specially designed equipment is used in a few large factories. The trays should not be overloaded, as the drying will be retarded and the curd will tend to lump. About 2 to 2½ pounds of the finely milled curd to each standard tray 30 by 30 inches will give satisfactory results under general factory conditions. Care should be exercised in stacking the trays evenly on the tray trucks. The bottom screen on the truck should be of finer mesh than the others, or else be covered with a cloth, to catch fine particles of curd that may sift through the other screens.

#### DRYING

Control of the amount and humidity of the air used for drying by means of a suitable inlet arrangement, control of the circulation of the heated air over and through the trays of moist casein by means of a sufficiently large high-speed fan, and careful regulation of the drying temperature used, are essential in the drying of all caseins. The casein should be dried and not baked. Dahlberg (3) recommends that with a drying temperature of 130° to 135° F., the heated air be supplied at the rate of 4 cubic feet per minute per pound of wet curd per hour going into the drier. When conditions are properly controlled, a temperature of from 125° to 135° will dry the casein in from 6 to 8 hours. However, if the drier is inefficiently constructed or operated, from 12 to 16 hours may be required. Usually it is not advisable to operate the drier at temperatures below 125°. Temperatures as low as 110° to 115° will cause uneven drying and discoloration of the casein if conditions are not properly controlled. Temperatures higher than 135° should not be used at the beginning or near the end of the drying period. If the temperature at the start is too high, a crust may form around the curd particles. This condition, known as "casehardening", causes uneven drying of the granules and is very detrimental to the quality of the product. Such casein is more slowly soluble and is poorer in quality than properly dried casein. At or near the end of the drying process evaporation is slower, and the nearly dried curd will quickly burn and become

brown or reddish brown in color if the temperature and flow of the hot air is not properly regulated. The drying process should be completed without interruption, and the heat should not be shut off before the casein is properly dried, as insufficient drying is favorable to growth of mold, and generally lessens the keeping properties of the casein.

A common factory arrangement for satisfactory drying is to have the fan located on top of the tunnel drier and preferably drawing the fresh air from a point near the ceiling. The fan forces the air past the heater coils and through the tunnel. The heated air in passing through the tunnel circulates between and around the loaded trays of moist casein and becomes laden with moisture evaporated from the moist curd. The moist heated air is discharged through an outlet flue to the outside of the building or partly recirculated. The amount recirculated through the drier is regulated by a damper arrangement or bypass. The dried casein preferably should not contain over 8 percent moisture. A moisture content much higher than 8 percent will adversely affect the keeping quality of the casein, since musty and foul odors and growth of molds will more readily develop.

#### GRINDING, PACKAGING, AND STORING CASEIN

The dried casein, upon removal from the drier, is usually dumped from the trays into a tight bin. This method of handling the dried casein is preferable to that of dumping it on the factory floor, practiced by some factories, as small sticks, and dirt particles are less likely to become mixed with the product. Sweepings from the drier or plant floor should be sold only as second-grade casein and should never be mixed with clean casein. If the dried casein is to be ground at the factory it should be allowed to cool to room temperature before being ground, to prevent gumming. Many manufacturers do not grind their casein but place it in sacks for shipment or storage as it comes from the drier. Whether the manufacturer, dealer, or user does the grinding, depends largely upon marketing conditions. Many of the larger dealers or jobbers blend caseins of different grades in their grinding process. These dealers perform a definite service, for by making a study of the formulas and requirements of the purchaser and by blending different grades and lots of casein to meet these conditions they are able to produce a satisfactory and uniform casein for particular needs. Separately, these lots of casein could not be satisfactorily used. Thus the casein jobber, by blending these caseins of widely different grades, creates a good market for caseins differing greatly in their properties. However, with such a system the manufacturer of good-quality casein may not receive as much for his product as he should on the basis of quality, while the manufacturer of poor-quality casein may receive a better price than its quality justifies. If manufacturing methods were standardized so that a more uniform product could be made there would be less need for blending, and casein from different plants could be sold more on its merits. The sale of casein on a merit basis would help to raise the average quality.

The casein manufacturer who has direct market outlets does his own grinding. When casein is ground to pass a 20- to 30-mesh

screen, it will meet most market requirements. Many of the larger factories are equipped with grinders which can be adjusted to deliver a product of any desired mesh. Whatever mesh is desired, the particles should be of even size. The dried casein should be screened after the first grinding. Only the oversize particles should be re-ground to avoid dusty casein.

The dried casein, either ground or unground, should be placed in clean dry sacks. Burlap sacks of 100 to 200 pounds capacity, lined with closely woven cloth or heavy paper, are satisfactory containers and are commonly used. One large manufacturer has adopted a heavy 3-ply paper bag as a marketing package. This bag complies with all shipping requirements of the railroads and has been well received by the purchasers of the casein.

The filled sacks should be tightly closed and then put in a dry, clean, storage room where a uniform temperature can be maintained. Wide variations in storage temperatures will cause the stored casein to sweat and then mold. If the casein becomes sufficiently moist, decomposition will take place. Vermin may also infest stored casein. When it is known before grinding that casein is to be stored for any length of time, it is best to store it unground, because unground casein will keep better than ground casein.

### LACTIC CASEIN

More lactic casein than hydrochloric or sulphuric casein is made in the United States. There is a more or less common preference for lactic casein among manufacturers, dealers, and users.

In order to determine the best method for making a uniform, high-grade, lactic casein the Bureau of Dairy Industry has, by experimental work conducted in the laboratory and on a commercial scale, developed improved methods for making it.

### METHODS OF MANUFACTURE

Most commercial lactic casein is made by the same general process, but the methods employed in different plants making lactic casein are not exact or uniform. In some plants the skim milk is allowed to sour naturally, but usually a starter is added to hasten fermentation. The skim milk is never allowed to coagulate into a solid mass if this can be avoided. When the skim milk has developed acidity enough to be at or near the coagulating point, the curd is "broken" or precipitated either by stirring or by heating with steam, or by both. The acidity of the skim milk at this point usually ranges from 0.5 to 0.6 percent. The length of time required for the skim milk to reach this acidity depends upon the kind and amount of starter added and the setting temperature, and varies from 2 to 5 hours.

Whey 2 or 3 days old, or whey saved from a previous batch and held under conditions favorable for rapid fermentation, is generally used as a starter, although in a few plants a skim-milk starter is utilized. The amount of starter used varies from 8 to 12 percent of the volume of skim milk to be processed, depending upon the condition of the skim milk as affected by such factors as the tempera-

ture and season of the year. The setting temperatures range from 95° to 100° F. as the minimum and from 115° to 118°, as the maximum. Methods of mixing the whey with the skim milk vary as well as methods of washing and temperatures of wash water.

There are a number of variations of the manufacturing methods just described which are used to a limited extent in making lactic casein.

Cooked-curd lactic casein is sometimes made. After the curd has been precipitated by direct steam at a low acidity (0.45 to 0.50 percent acid) and the whey drained off, the curd is covered with warm water, and the water and curd are heated to 160° to 180° F. This high temperature causes the curd to gather in a "rubbery", plastic mass. The curd is then packed in barrels where it settles into an almost air-tight solid mass, which, upon cooling, becomes very tough and hard. The filled barrels are then usually shipped to a central drying plant where the curd is ground and dried. When a green curd, either pressed or cooked, is shipped to a central drying plant it is usually paid for on the basis of dried casein obtained. Casein made from cooked curd has a high ash and free-acid content, is difficult to dissolve in the usual casein solvents, makes a heavy-bodied solution, and may be very unsatisfactory, depending on the purpose and method of utilization.

A semicooked-curd lactic casein can be made by bringing about precipitation with warm sour whey. The whey and skim milk are heated separately to a temperature of 130° to 135° F., and then mixed in a trough or mixing tank. The high precipitating temperatures produce a finished product with cooked-curd casein characteristics.

Several casein factories in the West have developed and are using a process of making lactic casein that produces a uniform product. This process consists in standardizing the amount of acid to be added in the form of starter at the time of setting. Then, by varying the setting temperature according to the acidity of the starter and skim milk, a very definite control of setting time is established. The acidity of the skim milk and that of the whey starter are determined. Enough whey starter is then added to the skim milk to bring the acidity to a definite end point (usually 0.25 percent acid). Exact setting temperatures have been worked out for various acidities of the skim milk. In actual practice, setting temperatures between 100° and 118° F. are used, depending upon the acidity of the skim milk. Coagulation takes place in approximately 2½ hours, and the curd settles after stirring and without further heating. The curd is then drained and washed.

#### QUALITY AND KIND OF STARTER NEEDED

In commercial practice often the selection of the starter is not given the proper attention. A contaminated starter or the wrong type of starter will affect the length of time that the skim milk will have to set before the desired acidity is developed. This is especially important where large quantities of skim milk are handled and the vat space is limited.

The ordinary lactic acid-producing starter, such as is commonly used in making commercial buttermilk, butter, or cottage cheese,

does not give as satisfactory results in making lactic casein as do special starters containing only organisms which produce relatively higher acidities. Of a number of high acid-producing organisms used in making starters for the experimental work on lactic casein, those in the culture employed in making concentrated sour skim milk proved most satisfactory. This culture contains bacteria of the *L. bulgaricus* type associated with a *mycoderma*. It readily produces about 2 percent acid in skim milk in 12 hours, when the skim milk is held at temperatures of from 105° to 108° F. These temperatures are too high for maximum acid development by the usual lactic acid-producing organisms. At lower temperatures the rate of acid development is slower.

The use of special starters is not always necessary, as high acid-producing organisms are naturally present in whey starters used by many lactic-casein manufacturers. It was found by determinations made in the field that the whey used for starter often contained from 1.7 to 2.4 percent of acid.

#### NEW METHODS

As previously indicated, when lactic casein is made by the methods just described, the acidity of the whey at the time it separates from the curd is less than the acidity that corresponds to the isoelectric point of casein (pH 4.6). Therefore, the conditions of precipitation are not the most favorable under these methods for the subsequent removal of substances other than casein from the curd, such as acid, milk sugar, and salts carried down in the curd. That is the main reason why so many samples of lactic casein have a higher ash and free-acid content than casein made by the grain-curd hydrochloric method. In the latter method, described elsewhere, dilute hydrochloric acid is added until the skim milk-acid mixture has an acid intensity of pH 4.1 and forms a granular curd of such character that thorough washing will eliminate most of the dissolved, occluded substances.

In experiments conducted to produce a lactic-type curd which would have the desirable properties of the grain-curd muriatic type, several methods were tried in order to learn how to develop sufficient lactic acid in whey or skim milk so that the acid whey or acid skim milk could be used as a precipitating agent like dilute hydrochloric acid. Experiments were carried on with a number of different starters to make a satisfactory starter which could be kept at room temperature and under factory conditions, and would produce a high degree of acidity in skim milk or whey within relatively short fermentation periods.

Lactic casein whey which was inoculated with a culture of high acid-producing organisms and held at room temperature (about 80° F.) overnight, had an acidity of 1.4 to 1.5 percent. When this whey was held for 1 or 2 days longer at room temperature, the acidity increased to from 1.7 to 2.2 percent with pH values of from 3.50 to 3.30.

The two following methods have commercial value and are, therefore, described in detail.

## DIRECT-PRECIPIATION METHOD

In the direct-precipitation method the skim milk is first heated to from 98° to 104° F. High-acid whey, which is made by allowing whey from a previous batch to stand at room temperature for from 2 to 4 days in order to develop a high acidity, is used as the precipitating agent. The high-acid whey should have a titratable acidity of 1.7 to 2.2 percent or a pH value of 3.50 to 3.30. There is no setting period. A quantity of the high-acid whey, weighing approximately one fourth as much as the skim milk to be processed, is slowly added with stirring to the skim milk. The correct amount to use ranges from 22 to 27 percent by volume of the skim milk, and depends upon such factors as the acidity of the high-acid whey, the temperature of the mixture, and the method of mixing. A clear green whey is obtained in the vat when the above amount of high-acid whey has been added, but the precipitated curd is soft and mats readily. As much whey as can be removed from the vat quickly is then drained off and more of the high-acid whey is added with steady stirring until bromocresol green indicator paper after being dipped in the whey is greenish-yellow in color, corresponding to a pH value of 4.2 to 4.1. The total quantity of high-acid whey added to bring the curd-and-whey mixture to the desired acidity ranges in volume from 30 to 35 percent of the volume of the skim milk. The actual proportion used depends chiefly upon the acidity of the high-acid whey and also on how much of the whey in the vat had been drained off. The curd is firm, resilient, and granular, and does not mat together. The whey is then drained off and the curd washed twice with water. The temperature of the first wash water should be from 85° to 95° F., and that of the second wash water about 60°.

Skim milk of high acidity was also used experimentally, but whey gave the better results. With the method outlined, the problem of providing containers for the whey that is to be used as the precipitating agent must be considered. This problem is especially important in the flush season. From 30 to 35 percent of additional vat capacity is required for fermenting the high-acid whey, and about 30 percent more vat space for precipitating the skim milk than with other methods. There are casein manufacturers who prefer to make lactic casein and normally do so, but on account of limited vat and floor space, make hydrochloric or sulphuric casein during the peak of the milk-production season. With this new method of making lactic casein, as there is no setting period, the extra vat space which normally would be required for setting is not necessary. Also, the expense of purchasing a commercial acid for use as a precipitant is eliminated, but in some plants where vat space is limited, the cost of providing extra vat space to ferment the acid whey is a consideration. Lactic casein produced by this method has many of the desirable characteristics of grain-curd hydrochloric casein.

## HOLDING METHOD

Clean, sweet, fat-free, skim milk, fresh from the separator is heated to from 95° to 100° F. and about 10 percent by volume of whey starter, which contains active, high-acid-producing organisms is added. The starter may be added before the skim milk is heated,

but in either case the skim milk should be stirred while the starter is being added to prevent partial, localized precipitation of the casein. Water-jacketed vats are desirable as it is easier to maintain a constant setting temperature than in unjacketed vats, but if the temperature is first raised to slightly higher than 100°, unjacketed metal vats or wooden vats will prove satisfactory. It is important, however, from the standpoint of maximum acidity developed and kind of curd produced, that the setting temperature be maintained at or near 100°. When an active starter is used and the proper setting temperature is maintained, the skim milk will have the desired acidity in 3 to 3½ hours. From 4 to 6 hours will be required when a less active starter is used.

The curd may be precipitated by either of two procedures. When the mixture of skim milk and starter has developed 0.55 to 0.58 percent acid, it will be near the coagulating point, and small flakes of curd can be detected by running the hand through it. The curd can be precipitated at this stage by stirring the mixture and heating gently, either with direct steam or with hot water in the jacket of the vat, to a temperature of from 104° to 106° F. The curd will be very soft, and unless stirring is continued for some time it will mat readily into a "mushy" mass. Temperatures above 106° will make the curd tough and rubbery.

The second and preferable procedure in precipitating the curd is to let the mixture of skim milk and starter reach an acidity of from 0.55 to 0.67 percent acid, in order to obtain a suitable coagulum. This coagulum should then be "broken" by stirring vigorously with the wooden rake or paddle provided for that purpose. Mechanical agitators could likewise be used. No heat should be applied at this stage. Ten to fifteen minutes' stirring will be sufficient to get a complete precipitation and a clear green whey. If the curd is not stirred it will be soft and mat easily.

In general commercial practice, an examination of the curd and tests of the whey with strips of bromocresol-green indicator paper will serve to indicate when the desired end point is reached, or the usual acidity determination may be made. If the indicator paper is employed the whey from the first method of precipitation usually imparts a color to the paper, expressed in terms of pH value, of from pH 4.85 to 5.00, while that from the second ranges from pH 4.70 to 4.80. Under ordinary commercial conditions, a pH value of approximately 4.75 will give the most satisfactory and uniform results.

It will be noted that thus far the procedure in making this type of lactic casein does not differ materially from that used in many plants. At this stage, however, instead of draining and washing with water, the curd is given a further treatment. After being stirred until a clear green whey has been attained, the curd is allowed to settle, and as much whey as can be removed quickly is drained off. Then whey, which has fermented from 2 to 4 days and contains 1.7 to 2.2 percent of acid, is added to the curd and whey left in the vat. The amount of high-acid whey required will depend upon its acidity and upon the amount of whey left on the curd, but enough should always be added and thoroughly mixed with the soft curd to produce a firm, granular, porous, and resilient curd and one that will

not mat when squeezed in the hand. The indicator paper should now be a greenish-yellow or yellow color, equivalent to pH 4.2 to 4.1, after being dipped into the whey. The character and "feel" of the curd is now very similar to that of the grain-curd hydrochloric type. With a little experience the maker can gage accurately the amount of high-acid whey to add to bring the curd-whey mixture to this desired end point. On the basis of the volume of the skim milk being processed, approximately 10 percent by volume of whey containing 2 percent acid will be needed; and with whey of a lower acid content, 15 to 20 percent may have to be added. It is important that the right amount be added to attain the desired acidity and consequently the correct condition of the curd. An excess of acid will produce a curd that will be hard to wash thoroughly, and an insufficient amount will not produce a curd of the desired resiliency and consistency.

When the desired end point has been attained the curd is ready to be drained and washed.

Barrels, milk cans, or an easily accessible tank will be satisfactory for holding the selected whey. The barrels or tank should be located in a warm place in the factory to facilitate acid development. They should be thoroughly cleaned when emptied.

Effective washing of the curd is very important. The final addition of the high-acid whey to produce a firm, granular, porous curd, adds to the amount of free acid present in the curd. The salts of the skim milk are more completely dissolved and thus more easily washed out, but insufficient washing, even with such a curd, will have a detrimental effect on the quality of the finished product. The curd should be washed at least twice. When the whey has drained away, the curd is trenched, water at a temperature of 85° to 95° F. is added, then the curd is stirred thoroughly, pushed back from the gate-valve end, allowed to settle, and the water drained off. The use of acidulated water for the first washing will facilitate the removal of the soluble salts. When more than two washings are given, it is preferable to use wash water at a temperature of about 85° to 95°, for all but the last washing. This last water should be cold, to help retard further acid development in the curd in the press. After the last wash water has been drained off, the curd should be pressed, milled, spread, dried, and packed. These steps have already been described.

#### SULPHURIC CASEIN

Sulphuric casein is made to a large extent in plants which make casein only for a brief period in the season of flush production of milk. In some plants which normally make lactic casein, sulphuric casein is made during the flush season when vat space is too limited to make lactic casein from all the skim milk that is available. Practically all dairy-products plants have sulphuric acid on hand, as it is used in making butterfat determinations. It is cheaper than hydrochloric acid. Sulphuric acid with a specific gravity of 1.83 is used. It can be purchased from any dairy-supply company in carboy lots. Pressed-curd and cooked-curd sulphuric casein are the two types most commonly made.

## PRESSED-CURD SULPHURIC CASEIN

In making pressed-curd sulphuric casein the fresh skim milk is heated to from 115° to 125° F.; 120° is the temperature most commonly used. Excessive foam should be avoided. Usually the foam on the skim milk in the vat is scraped off with a board or rake before the acid is added. The commercial acid before use is diluted with four or eight times its volume of water. Special precautions are necessary to avoid accidents in diluting the sulphuric acid with water. The acid should always be carefully added to the water, and not the water to the acid. The diluted acid is slowly added while the skim milk is constantly stirred, until a clear separation of curd and whey occurs. This requires but a few minutes. No very definite end point is attained. A clear green whey with the curd separating cleanly is desired. The curd is in large masses that mat readily and is tough and stringy. The whey shows an acidity of 0.35 to 0.40 percent when titrated in the usual manner.

The curd is pushed back from the gate-valve end of the vat and allowed to settle for a few minutes, and the whey is quickly drained. The curd is then washed. Cold water is preferable as it tends to grain the curd and prevent matting. In order to obtain effective washing, it is necessary to hand-shred the curd. Two or three washings are recommended. After being washed, the curd is ready to be pressed.

## COOKED-CURD SULPHURIC CASEIN

The method of making cooked-curd sulphuric casein does not differ materially from the pressed-curd method. A precipitating temperature of 120° to 125° F. is used and just enough diluted sulphuric acid (4 to 8 parts water to 1 part acid) is added to bring about a clear separation of the curd. The acidity of the whey should not exceed 0.34 percent acid and ranges from 0.32 to 0.34 percent. The curd is doughlike in character and forms in large masses and is stringy and tough. The whey is quickly drained away, then warm water is added, and the curd and water are heated with direct steam to a temperature of from 160° to 180°. This high temperature causes the curd to gather together in a semifluid, plastic, doughlike mass. After the water has been drained off the curd is cut into slabs and packed in barrels. Upon cooling it becomes very tough and hard. Such a curd is not pressed, but when cool is ground and dried. On account of the toughness of the cooked curd, a special mill of greater strength than the ordinary mill is required.

The cooked curd does not produce a high-grade casein although it is perhaps suitable for a few limited uses. The cooked-curd casein dissolves with difficulty in the usual casein solvents, its solutions are heavy-bodied, and it will invariably be relatively high in ash and free-acid content. It may have an attractive appearance when dried, but does not possess the desirable properties that the user of high-grade casein demands. The high precipitating and washing temperatures are detrimental to the quality of the finished product. High temperatures at any stage of the casein manufacturing process are, in general, harmful to the production of a high-quality product.

## OTHER METHODS OF MAKING SULPHURIC CASEIN

There are a number of variations of manufacturing methods in commercial use for making sulphuric casein. Either lower or higher precipitating temperatures than those given are occasionally employed. Smaller amounts of acid and greater dilutions are also used. Sulphuric acid can be substituted for hydrochloric in making a grain-curd casein or in special processes. For best results in making grain-curd casein it is imperative that, when sulphuric acid is the precipitating agent, a properly diluted acid be used. Hydrochloric acid, with a specific gravity of 1.15, when diluted with 8 parts of water to 1 part of acid has about the same normality or strength as sulphuric acid, with a specific gravity of 1.83, which has been diluted with 30 parts of water. Dilution of the sulphuric acid with at least 30 parts of water was found necessary in order to make a satisfactory grain-curd sulphuric casein. A dilution of from 40 to 50 parts of water to 1 of sulphuric acid will give even better results. The sulphate salts produced when sulphuric acid is the precipitating agent are less soluble than chlorides, and especially effective washing is necessary in order to obtain a low ash and free-acid content in the finished product. Also, the precipitating temperature required in making grain-curd sulphuric casein is slightly ( $2^{\circ}$  to  $4^{\circ}$ ) higher than that required in making grain-curd hydrochloric casein.

## HYDROCHLORIC (MURIATIC) CASEIN

Hydrochloric (muriatic) casein is made in a number of the larger casein factories in the United States, where the whey is usually utilized for recovery of milk sugar, or lactose. Hydrochloric-casein whey is more suitable for the manufacture of milk sugar than either lactic or sulphuric casein whey, because the sugar content of the skim milk has not been diminished by fermentation as under the one method, and sulphates, which are difficult to remove in refining the milk sugar, are not present as under the other method.

The use of hydrochloric acid also has advantages over sulphuric acid in the character of the curd formed as previously explained. The calcium and other mineral substances carried down with the curd in the form of chlorides are more soluble and therefore more easily removed in washing than the sulphates formed when sulphuric acid is the precipitant.

The three principal types of hydrochloric casein made commercially are pressed-curd, cooked-curd, and grain-curd hydrochloric casein. No setting period is required. Fresh skim milk is heated to different temperatures, depending upon the type of curd manufactured and the practice of the plant. The amount of hydrochloric acid added, and the dilution of the acid before it is used, varies greatly in different plants. While chemically pure (c.p.) hydrochloric acid can be used in making casein, it is not often used for this purpose, on account of its relatively high cost as compared with the acid of commercial grade commonly known as muriatic acid. Muriatic acid with a specific gravity of 1.15 (Baumé  $20^{\circ}$ ), which contains about 35 percent hydrochloric acid, is generally used. Muriatic acid can be purchased from most chemical companies in single carboys, carboy lots, or in tank-car lots, as desired.

## PRESSED-CURD HYDROCHLORIC CASEIN

The method of making pressed-curd hydrochloric casein is similar to that used in making pressed-curd sulphuric casein. Fresh skim milk is heated to approximately 120° F. Any foam on the heated skim milk is removed before the acid is added. Commercial acid (35 percent hydrochloric) is diluted by mixing 2 to 3 parts of water with 1 part of acid. The diluted acid is slowly added to the skim milk with constant stirring until a clear separation of curd and whey occurs. This separation and the formation of a clear green whey require only a few minutes. The curd is physically similar to that obtained in making pressed-curd sulphuric casein. The curd is drained, washed, pressed, and dried as in making other types of casein.

## COOKED-CURD HYDROCHLORIC CASEIN

In making cooked-curd hydrochloric casein, the method of firming and handling the curd, is almost identical with that used in making cooked-curd sulphuric casein. Less of the cooked-curd hydrochloric casein is made, however, than of cooked-curd sulphuric casein. The finished casein is not quite so readily soluble in casein solvents and its solutions are somewhat more viscous than those of the latter type.

## GRAIN-CURD HYDROCHLORIC CASEIN

Grain-curd hydrochloric casein is a type of casein made by a method developed in the Bureau of Dairy Industry (2). It is so called because in its manufacture the curd forms in small grainlike particles. The mass of curd does not mat together but maintains a granular and porous texture. This makes possible effective washing of the curd and the removal of substances which lower the quality of the finished product.

Grain-curd casein when properly made meets the requirements of users who must have a high-grade product. The manufacturing methods are such and can be so controlled that a product of uniform quality can be readily produced.

Fresh skim milk is heated to from 93° to 96° F., depending upon its acidity. For best results, skim milk that has an acidity of not more than 0.15 to 0.16 percent lactic acid should be heated to 96° and skim milk with an acidity of 0.20 or 0.21 percent should preferably be heated to 93° or 94°. Close control of the precipitating temperature within these limits is essential to obtain a firm, granular curd. A temperature above 96° when the ordinary vat method is used, tends to make a coarse, lumpy curd, and a temperature below 93° gives, a soft, fine curd, both of which are detrimental to the product. After the skim milk has been thoroughly stirred and heated, the foam should be scraped off with a suitable board or level before the acid is added, as foam tends to make a floating curd.

There are two important factors to consider in adding the acid to the heated skim milk—namely, the dilution and the method of adding. The muriatic acid should be diluted by mixing 8 to 10 parts of water with 1 part of acid. The dilute acid should be added slowly in a spray or fine stream to the skim milk, which should be stirred gently and constantly to insure even distribution of the acid

and to prevent localized precipitation. If the mixture of skim milk and acid is not stirred, the curd will form uneven masses. Very fast stirring or a temperature below 93° F. gives too fine a curd, which tends to float, is hard to drain and wash properly, and causes mechanical losses in processing and foaming in the finished product. Too slow stirring or a temperature above 96° gives a coarse, lumpy curd which is difficult to wash effectively. When the curd begins to "break" or settle in the vat, it is important that stirring be continued until the whey is clear, or practically all of the curd has been precipitated. The curd, however, is still soft and mushy, and more of the dilute acid should be added slowly until the whey has an acid content corresponding approximately to pH 4.1 in a color test with bromocresol green paper, or 0.50 percent acid by titration. The total amount of concentrated acid required is affected slightly by the percentage of lactic acid in the skim milk; the casein content of the milk, which varies with the breed of the cows and the season of the year and the feed given the cows, the precipitating temperature, and various other factors. Approximately 2.4 to 2.6 quarts of concentrated acid with a specific gravity of 1.15 per 1,000 pounds of fresh skim milk will usually be needed. The correct end point, expressed in titratable acidity, may range from 0.47 to 0.53 per cent acid, but it will normally be 0.50 percent.

When the correct end point is reached, the curd will have a characteristic "feel" and appearance. The curd is firm, porous, resilient, and will not mat when squeezed together in the hand. With a little practice the maker, by examining the curd, can gage this point rather accurately and consequently determine when the right amount of acid has been added. Insufficient acid gives a milky, soft curd that breaks up easily in washing and reduces the yield. An excess of acid causes a gelatinous sticky layer to form over the curd particles, which retards thorough washing and injures the texture. Some of the whey may be drained off before the correct end point is reached. Slightly less acid will be required when this is done. The correct end point should be attained as soon as possible and the curd drained and washed quickly for best results.

Effective washing of the curd is very important in making grain-curd casein as in making other types of casein. The curd should be washed at least twice and preferably three times. The best temperature for all except the last wash water is 94° F. About as much water is added to the curd as there was whey in the vat, the curd is stirred thoroughly, and the water drained off. This operation is repeated once or twice. The use of water that is much cooler than 94° in the first washing, tends to soften the curd, causes it to stick to the press cloths, and retards drainage in the press. The use of water that is too hot tends to cook the curd and to make the finished casein more insoluble. Either extreme should be avoided. The last wash water, if desired, may be cooler; water with a temperature as low as 60° is often used in the final washing. It is advisable to acidulate the first wash water by adding hydrochloric acid at the rate of about 100 cc of acid to 1,000 pounds of water.

The curd is now ready to be placed in the press, and is handled throughout the rest of the process according to the usual methods.

## OTHER METHODS OF MAKING HYDROCHLORIC CASEIN

A few large manufacturers of hydrochloric casein are able by using a beater to break up the curd before it is washed, to produce a high-grade casein at higher temperatures and lower dilutions of the acid than are ordinarily used. The formation of the curd is brought about at a temperature of  $104^{\circ}$  F., or even higher, by the addition of acid diluted with 2 or 3 parts of water to 1 part of acid. The coarse, lumpy curd thus obtained is broken by the beater into particles small enough to wash properly. Practically the same results, so far as the quality of the finished product is concerned, are obtained as when a precipitating temperature of  $93^{\circ}$  to  $96^{\circ}$  is used. With the higher precipitating temperature of  $104^{\circ}$  or more, the end point obtained is nearer the isoelectric point of casein than in the

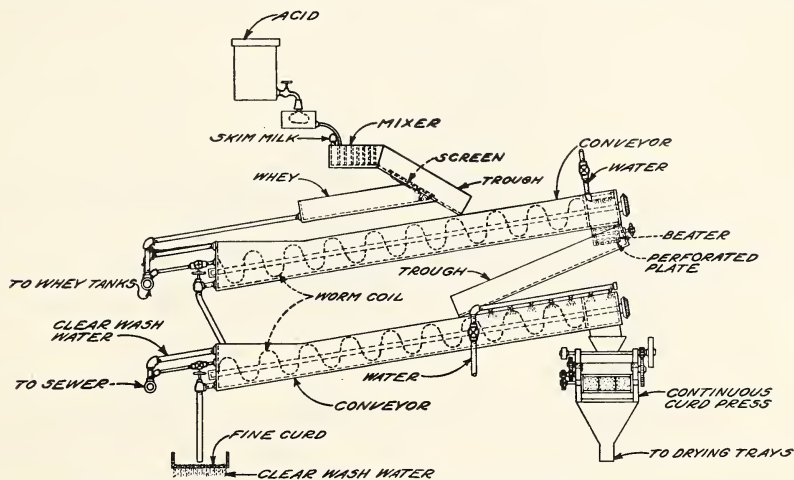


FIGURE 5.—Sheffield continuous process. Requires only one man to isolate, wash and press the curd from skim milk available in the largest casein plants.

usual grain-curd process. In terms of titratable acidity, the whey contains from 0.44 to 0.46 percent acid.

The Sheffield continuous process (fig. 5) has received a good deal of attention in recent years. It is patented and cannot be used without the payment of a royalty. A high-grade product is made which commands a premium price on the market. The method is worthy of consideration by companies which process large amounts of skim milk daily, because of the saving in time and labor as compared with the vat process (fig. 6).

The method is briefly as follows: Fresh skim milk from the storage tank is warmed to  $110^{\circ}$  F., by means of a tubular heater, and is pumped direct to a small, specially arranged mixing apparatus where hydrochloric acid, diluted with 3 or 4 parts of water to 1 part of acid is added directly to the skim milk, and precipitation is accomplished quickly. The arrangement for mixing is important. The flow of the skim milk and dilute acid is regulated as they enter the mixer so as to obtain quickly an end point which is nearer the isoelectric point than that attained in ordinary grain-curd methods. The higher precipitating temperature used produces a coarse, stringy,

lumpy curd. The mixing and shredder devices, which are important parts of this process all combine, however, to make this higher end point feasible and practicable. The curd and the whey pass around baffle plates in the mixer, and from the mixer they flow along a trough, which has a screen in the bottom, toward an inclined screw conveyor of suitable construction. Most of the whey filters through the screen and so is quickly removed from the curd. The whey that does not pass through the screen flows by gravity to the lower end of the screw conveyor and is removed by means of an overflow pipe. At the upper discharge end of this first conveyor the curd is forced through a coarse screen by means of a beater arrangement, and moves thence to the second inclined conveyor where it is washed thoroughly. From the last conveyor the thoroughly washed and cooled curd passes continuously through a press, and is then dried by means of a revol-

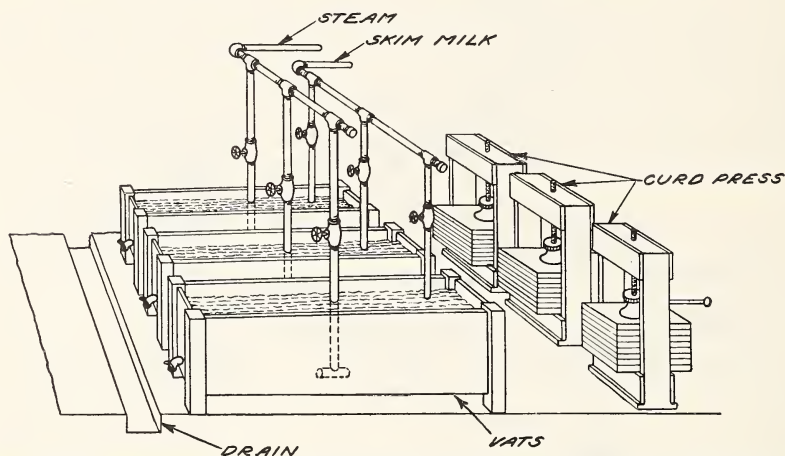


FIGURE 6.—The vat method. Requires a longer time and more expense for labor than the continuous process.

ing drum drier. The complete process requires approximately 21½ hours from the time the skim milk and acid are mixed until the casein is pressed, dried, ground, bagged, and ready for shipment. When the facilities afforded by this system are properly utilized, the manufacturer is practically assured of a finished product that will be low in ash, free-acid content, and foam-producing properties, provided the correct end point is reached in the precipitating process and the right temperature is employed. While primarily intended to be used in the making of hydrochloric casein, this process can be adapted to the making of both lactic and sulphuric casein.

### YIELD OF CASEIN

The amount of casein in skim milk varies within a rather narrow range depending upon the breed of cow, lactation period, and other factors. Three percent, however, is commonly considered as the amount in cows' milk obtained from mixed herds. The casein content of skim milk in terms of percentage is slightly greater than that of the whole milk from which it is obtained. The yield of com-

mercial casein per hundred pounds of skim milk depends upon the methods employed for recovering it as well as upon the solids content of the skim milk.

Inadequate washing of curd results in a greater yield of finished product than if the curd is washed effectively, as the mechanical loss of casein is smaller and more of the impurities are left in the final product. Such an increase in yield is obtained at the expense of quality. The yield of high-grade casein that can be expected from a granular, well-washed curd will range from 2.6 to 2.9 pounds per 100 pounds of skim milk processed. With a coarse, lumpy, difficultly washed curd, the yield may be 0.2 to 0.3 pound greater than these figures, but the product is of lower grade.

Milk produced during the winter will usually yield 0.2 to 0.3 pound more casein per 100 pounds of skim milk processed than milk produced in the summer. Records from one large manufacturer show that under the same method of operation the yield was 0.3 pound greater in January than in July, and other manufacturers report about the same difference. Variations in acid dilutions, speed of mixing, method of removing foam, and method of washing are additional factors which affect yield.

A maximum yield is naturally desirable from an economical standpoint. Too often, however, maximum yield is obtained only by sacrificing quality. Many plants could greatly improve the quality of their finished product, if the highest yield consistent with producing quality casein was the objective, rather than the highest yield without regard to quality.

## USES

The uses of acid-precipitated casein are wide and diversified. Its adhesive and water-resistant properties are recognized in the variety of ways in which it is utilized. It is employed to some extent in the paint industry, especially in the preparation of cold-water paints; as a base for insecticide sprays; as a filler for certain cloths; in the processing of such articles as leather and linoleum; and in many other industries. The two principal uses of acid casein, however, are in the coated-paper and glue industries. More commercial casein is utilized in the coating of paper than for all other purposes combined. Its function is to bind clay and other material to the paper stock. Coated paper has a superior printing surface and takes color tones much better than uncoated paper.

Casein is used to a considerable extent in the making of water-resistant prepared veneer glues. Some manufacturers buy casein direct from a jobber or manufacturer and make their own glues. In this way they are able to modify formulas for particular needs.

In its commercial utilization casein is first dissolved in an alkali; hydrated lime is the solvent commonly used in the glue industry, and soda ash, trisodium phosphate, borax, and ammonia in the coated-paper industry.

## MARKETING

The sales value of commercial casein is dependent upon the same general factors that govern the sales value of other manufactured products, and especially upon supply and demand, the physical and

chemical properties desired, the uniformity of the product, the reliability of the manufacturer, the use to be made of the product, and its presentation to the trade in an attractive sales package. As the user becomes more appreciative of the value of high-grade casein, the manufacturer of such casein will have a big sales advantage over the manufacturer of an inferior casein. There seems to be a very definite trend on the part of certain large users of casein toward more exacting specifications. They are willing to pay a better price for high-grade casein than for casein of inferior quality. This is a very encouraging condition, for too often in the past the buyer and the user have been interested primarily in the purchasing price, quality being only a secondary consideration. With both casein maker and user becoming conscious of the importance of quality, the sales value of high-grade casein should be enhanced.

As the value of casein depends so much on its physical and chemical properties, the manufacturer or prospective manufacturer should be familiar with them in order to be able to make a finished salable product which possesses as many of these desirable properties as possible.

Casein cannot be judged for quality merely by its appearance or by a physical examination. Exact methods are necessary to determine accurately the fitness of casein for the purpose intended. Some of these will be described later. Casein, however, possesses certain physical characteristics that can be used as an indication of whether the product has been properly made and handled. It should be uniform in color, clean, and free from objectionable odors and burned particles. The color should be a very light yellow or creamy white. The unground casein should be porous, crumbly in appearance, and not hard or glossy. A poor casein usually appears dull and often grayish in color, in contrast to the bright, even color of good casein. When ground it should be uniform in particle size and not dusty. The maker of casein should consider these indications of good quality in preparing his product for market.

Casein for most purposes should be clean, low in free-acid, fat, and ash content, dissolve completely within certain limits of alkalinity and temperature, have good adhesive strength, and be free flowing when dissolved, and for paper coating spread easily without foaming. To determine accurately whether a casein is adapted to the purpose intended and the most equitable price that can be paid under the market conditions, actual utilization tests should be made. Then the manufacturer, to obtain the best price for his product in the future, should if necessary modify his manufacturing methods to supply casein that will comply with the user's requirements.

Casein is commonly sold through a dealer or jobber in carload lots. The small manufacturer is often handicapped by inadequate storage facilities and so must sell to a dealer. Such dealers have established contacts with the trade and are usually in a better position to market casein to advantage than is the individual manufacturer. From observations made in various sections of the country in 1931, it was found that the difference in prices paid the manufacturers ranged from 3 to 8 cents per pound. The manufacturer must be familiar with reliable current quotations in order to market his casein to best advantage.

Some manufacturers contract to sell their year's output at a definite price. Such an arrangement is satisfactory when the contract is elastic enough to protect both parties from taking undue advantage of each other. Casein prices fluctuate within rather wide ranges, and where a definite price is set for a year in advance one or the other of the contracting parties may find such an agreement undesirable. A flexible contract based upon market conditions would be fairer to both dealer and manufacturer.

Where the dealer is reliable and a fair price is paid, such a system of selling casein is probably more conducive to orderly marketing than is an attempt on the part of a large number of small manufacturers to market direct to the user. As casein is usually sold in carload lots and a uniform product is desired, and the small factories use a variety of manufacturing methods, they are hardly in a position to adequately supply such demands. The popularity with the trade of much of the imported casein formerly used in this country was due not so much to any superior quality as to uniformity. This uniformity was due to a system of grading and blending previous to exportation. As uniformity is demanded by the user, the adoption of standardized manufacturing methods, together with a good system of grading, would seem to be highly desirable on the part of domestic manufacturers.

The large manufacturer of casein is in a much better position than the small one to market direct to the user. Usually in large plants the manufacturing methods are watched more closely and the product is more uniform than in small plants. Then too, a large producer is better able to establish good trade contacts. A familiarity with reliable market outlets should first be acquired, however, before direct marketing is attempted. A few large casein manufacturers have sales representatives to whom commissions are paid when sales are made.

New, clean sacks should be used. When more than one type of casein is made, each type should be appropriately labeled. The sales value of a good-quality casein, made by approved manufacturing methods and having the properties demanded by the user, will be increased if it is attractively packaged.

## METHODS FOR DETERMINING THE PROPERTIES OF COMMERCIAL CASEIN

The importance of manufacturing casein so that it will have certain desirable properties has been stressed. The following methods are recommended for determining these properties. It is essential that a representative sample be used in each determination.

### MOISTURE CONTENT

Approximately 1 g of casein is weighed into a tared silica or platinum dish and dried in a vacuum oven for 5 hours at 98° C. The sample is cooled in a desiccator and dried 1 hour longer, then cooled and weighed; this operation is repeated until the weight is constant. The percentage of moisture is then calculated. The dry sample can be used for the ash determination.

## ASH CONTENT

If the sample contains less than 2.5 percent of ash, the addition of calcium in the form of calcium acetate is necessary to prevent volatilization of organic phosphorus during the ashing process. Therefore, to prevent possible loss of phosphorus, 2 cc of approximately tenth molal calcium acetate solution (equivalent to 0.0112 g of calcium oxide) should be added to the 1-g sample of casein, and the sample charred over a microburner without being allowed to burst into flame. The exact amount of calcium oxide added must be known, and must be subtracted from the weight of the ashed sample and container, before the percentage of ash is calculated. Ignition is completed in a muffle, giving a white ash. The addition of 1 cc of chemically pure nitric acid to the charred material is recommended as an aid in reducing it to ash. It is difficult to get a white ash without the addition of nitric acid. With some caseins it may be necessary to use 2 cc of nitric acid. The acid is then evaporated over a low flame before the charred sample is placed in the muffle. In calculating the percentage of ash no correction is made on account of the nitric acid used, as the acid contains few, if any, salts.

## ADHESIVE STRENGTH

Twenty g of casein are weighed into a previously tared beaker, which contains a stirring rod. About 70 cc of water is added to the casein in the beaker, and its contents are allowed to stand with frequent stirring for half an hour. Then 2.4 g of powdered, chemically pure borax is added, and the mixture is warmed and stirred until solution is complete. Some caseins may require more borax to dissolve completely. It is essential that the mixture diluted with a few cubic centimeters of water shall turn an alcohol solution of phenolphthalein pink. When solution is completed enough water is added to make the total weight of the solution 100 g. Each 5 g of the solution then contains 1 g of casein.

One hundred g of dried clay is weighed into a casserole supplied with a blunt instrument for crushing lumps and mixing. A standard clay should be used. Kaolin, Special for Tannin, has been found satisfactory. Seventy cubic centimeters of water is added and the whole mixed to a smooth paste. The casserole and contents are then counterbalanced and 30 g of the casein solution weighed in. After thorough mixing, a small amount of the mixture is spread on a sheet of paper by means of a straight-edged brass scraper or camel's-hair brush. The sheet is marked "6 grams", denoting the number of grams of casein, and put aside to dry. The casserole is again balanced, and 5 g more of the casein solution is weighed in. The mixing and coating are repeated, and this sheet is marked "7 grams." Increments of 5 g of the casein solution are added, and coatings are made up to "12 grams."

The coated papers are allowed to become thoroughly dry. Then, by holding them to the light, sections of uniform thickness are selected and marked. Sticks of good-quality sealing wax are well softened in a flame and pressed on the selected areas. Thirty minutes is allowed for the wax to cool. Then the fingers are placed on the paper beside the wax and the stick lifted with a steady pull. If the coating comes

away without pulling any of the fibers of the paper, the test is negative. If the whole surface of the paper is pulled away, the test is positive. If part of the fibers are torn, the test may be considered as being on the border line.

High-grade caseins will give positive tests on the sheets marked "7 grams", "8 grams", or "9 grams." A casein which does not pull until the sheets marked "11 grams", or "12 grams" is reached is distinctly inferior in strength.

Since the result is affected by differences in the clay and in the paper used, it is important that the same grade of clay and type of paper be used consistently.

The quantities of clay, casein, etc., mentioned may be halved, if desired, provided the amount of mixture used for each separate coating is kept small.

### SOLUBILITY

A rough idea of the solubility of casein may be obtained in making up the solution for determining the strength. The following method is more sensitive: Solutions of borax and water are made up which contain 24, 30, and 40 g of borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) per liter, and are labelled "12 percent borax", "15 percent borax", and "20 percent borax", respectively. Fifty cc of the 12 percent solution are added to 10 g of 20-mesh casein, the mixture stirred and placed in a water bath at 65° C. It is stirred continuously for 5 minutes, and then at 10 minutes, and at 15 minutes. If the casein is completely dissolved, it may be reported as "soluble in 12 percent borax"; otherwise the test should be repeated with another 10-g portion and the next higher concentration of borax. If this portion is not entirely dissolved, a third portion is tried with the 20 percent solution. Only extremely poor caseins are insoluble in the 20 percent borax solution. Frequently all of the sample will be dissolved except a few difficultly soluble particles. One cause of these insoluble particles is believed to be foam on the milk during precipitation.

### VISCOSITY

A great variety of methods have been employed to determine the viscosity of casein solutions. These methods have involved the principle of time of efflux from a standard orifice, or else the torsion of a wire caused by the resistance of the casein solution to the rotation of a plunger. The methods that seem to be in most common use for determinations on commercial, acid-precipitated casein, express the viscosity in relative rather than in absolute units. However, while some time and effort may be required to set up and standardize equipment for the determination of the viscosity in absolute units, such equipment is well worth while because of the ease with which the determination can be made, the accuracy of the results, and the fact that they can be expressed in definite units to which reference and comparison may be made.

One of the viscosimeters which may be used for accurately determining the viscosity of the fluid material is the burette consistometer (1, 4). The fundamental principle of its use is that a series of observations are made at different rates of flow in a capillary by

varying the hydrostatic head. The determination in poises at different heads rather than at one head, is a check on the accuracy of the determination. If the consistometer has been standardized, and the constants for the different heads have been determined, it is necessary only to multiply the constant of the head used by the time in seconds required for a unit amount of the casein solution to pass through the capillary, to obtain the viscosity of the solution in poises.

Casein solutions change in viscosity with time; the viscosity is also affected by the solvent employed, the reaction or pH value of the solution, and the temperature of the solution. Therefore, it is necessary to standardize the entire procedure if comparable results are to be obtained.

The relative viscosity of casein solutions may be obtained by allowing definite amounts of the solutions, which have been made up in a similar manner, to flow through a standard orifice under a comparable head in each determination. This method is not as accurate and in other respects is not as satisfactory as the use of a burette consistometer.

Some judge the viscosity or fluidity of casein solutions simply by observation, but it is impossible to do this with any degree of certainty, because an opaque, creamy solution may look viscous and actually have a low viscosity, whereas a transparent, watery-looking solution will often have a comparatively high viscosity.

#### ACID INTENSITY—pH VALUE

The pH value of casein may be determined as follows: About 2 g of casein, 2 cc of distilled water, and a few crystals of quinhydrone, are thoroughly mixed in a small mortar. A portion of the mixture is forced into a  $\frac{1}{2}$ -inch length of  $\frac{1}{4}$ -inch glass tubing, and a gold-wire electrode is inserted half-way through the casein plug. The other end of the plug is placed in contact with a saturated solution of potassium chloride which forms the bridge of a potentiometer outfit, and the determination of pH value is completed as is customary in the quinhydrone method (6.)

#### FREE-ACID VALUE

Ten g of 20-mesh casein is mixed thoroughly with 100 cc of water, and the mixture is allowed to stand for an hour with occasional stirring. Fifty cc of the supernatant solution is then titrated with tenth-normal sodium hydroxide. Phenolphthalein solution is used as the indicator. The solution should be stirred while it is being titrated, and the alkali slowly added until a faint pink color persists throughout the liquid. The free-acid value is expressed as the number of cubic centimeters of alkali solution required in the titration. An effectively washed casein will require less than 4 cc.

#### FAT CONTENT

A number of methods for determining the fat content of casein have been published. It is not known which one is best.

Sutermeister (5) describes a method which is a modification of the Babcock method and is much more rapid than procedures which

involve the use of organic solvents. It gives results which are higher than those obtained by the ether extraction of the solid casein. Two g of casein is soaked in 6 cc of water in a small beaker about one half hour; then with constant stirring, 9 cc of concentrated sulphuric acid (specific gravity 1.84) is added. This solution is poured into the Babcock skim-milk test bottle, the beaker is rinsed with 5 cc of water and 5 cc of sulphuric acid, and the washings poured into the test bottle. Then the bottle is filled to the base of the neck with dilute sulphuric acid (4 cc of water and 5 cc of concentrated acid) and whirled in the centrifuge for 5 minutes; filled to the top of the graduated portion of the neck with dilute acid, whirled 2 minutes, and the fat column read while still hot. The length of the fat column as read on the graduated neck, when multiplied by 9, gives the percentage of fat in the casein.

#### FOAMING TENDENCY

Foaming of clay-casein slips during their application to paper is probably the most troublesome difficulty experienced in commercial paper coating. The method that has been used by Whittier, Gould, and Hall (8), of the Bureau of Dairy Industry, for determining the foaming tendency of casein, is essentially that of Richards.<sup>2</sup>

A 110-volt 60-cycle alternating current 1/15-horsepower synchronous motor mounted with shaft vertical and operating at a speed of 1,800 revolutions per minute, was used. The stirrer was mounted on the end of a round shaft one fourth of an inch in diameter and 4 inches long, and consisted of a blade  $1\frac{3}{8}$  inches long horizontally, one fourth of an inch wide vertically, and one thirty-second of an inch thick. The stirrer and shaft were plated with nickel.

The slips were prepared by softening 11 g of casein in 55 cc of water adding one half of a gram of soda ash, heating the solution to 50° C. and mixing with a suspension of 100 g of clay (Kaolin, Special for Tannin) in 100 cc of water. The dry clay had been sifted through a 40-mesh sieve before being used.

One hundred cc of the slip was poured into a 100 cc graduate, and the graduate and its contents were weighed. Two hundred g of slip was then placed in a 400 cc low-form beaker, the motor-driven stirrer placed so that the top of the blade was three fourths of an inch below the surface and the stirrer run for 5 minutes. After standing for 1 minute, 100 cc of the slip was poured into the same 100 cc graduate as before, and the graduate and the contents were again weighed. The difference between the weights of 100 cc before and after being stirred is a measure of the foaming tendency and is called the foaming index.

Little can be learned about the properties of casein by its appearance, other than the amount of foreign material and burned particles present, and the size and uniformity of the particles. Particle size affects color. Differences in the color may best be determined by examining solutions.

Methods for determining other properties may be obtained from the Bureau of Dairy Industry, United States Department of Agriculture, Washington, D.C.

<sup>2</sup> RICHARDS, C. W., Chemist, Oxford Paper Co., in unpublished paper on file in the Bureau of Dairy Industry.

## CONCLUSIONS

Manufacturing methods are described which will aid greatly in producing uniformly high-grade casein, which has such desirable properties as low ash and free-acid content. For most purposes, high-grade casein made by the various methods described is interchangeable. It is by no means certain, however, that the product will be satisfactory to all consumers and for all purposes. There are many uses for acid-precipitated casein, and others will doubtless be found. Some of these uses require caseins of different properties.

Casein has been made for a number of years by milk-products plants throughout the United States, but its manufacture has often been started solely as a means of obtaining some return for surplus skim milk. As a result there is great variation in the quality and uniformity of casein produced. Likewise, there has been but little attention given to methods for determining the properties of casein.

There are variations in the methods of utilization when the casein is used for the same purpose. Casein which is not satisfactory when used under one set of conditions may be satisfactory after these conditions have been changed to bring about greater operating efficiency. This state of affairs emphasizes the need in the casein industry of a better general knowledge of methods for determining the properties of commercial casein, and of the requirements of consumers.

The application to commercial practice of the manufacturing methods recommended herein, together with a wider use of the analytical methods described, will greatly improve the quality and uniformity of domestic casein.

## LITERATURE CITED

- (1) BELL, R. W., and GOULD, S. P.  
1931. PROPERTIES OF ACID CASEINS. *Jour. Dairy Sci.* 14: 337-346.
- (2) CLARK, W. M., ZOLLER, H. F., DAHLBERG, A. O., and WEIMER, A. C.  
1920. STUDIES ON TECHNICAL CASEIN. II. GRAIN-CURED CASEIN. *Jour. Indus. and Engin. Chem.* 12: 1162-1163.
- (3) DAHLBERG, A. O.  
1927. THE MANUFACTURE OF CASEIN. In Sutermeister, E., *Casein and Its Industrial Applications*. Ch. 3, p. 67-68, illus. New York.
- (4) HERSCHEL, W. H., and BULKLEY, R.  
1927. CALIBRATION OF THE BURET CONSISTOMETER. *Indus. and Engin. Chem.* 19: 134-139, illus.
- (5) SUTERMEISTER, E.  
1929. *CHEMISTRY OF PULP AND PAPER MAKING*. Ed. 2, 565 p., illus. New York and London.
- (6) WATSON, P. D.  
1927. USE OF QUINHYDRONE ELECTRODE FOR FOLLOWING CHANGES OF PH IN SWISS CHEESE. *Indus. and Engin. Chem.* 19: 1272-1274, illus.
- (7) WHITTIER, E. O.  
1931. BROMOCRESOL GREEN PAPER IN THE MANUFACTURE OF GRAIN-CURED CASEIN. *Jour. Dairy Sci.* 14: 26.
- (8) ——— GOULD, S. P., and HALL, S. A.  
1933. CAUSES AND PREVENTION OF FOAMING IN CLAY-CASEIN SLIPS USED FOR PAPER COATING. *Indus. and Engin. Chem.* (In press.)